radiative (k_r) and nonradiative (k_{nr}) are constants for excited-state decay. Values of k_r are nearly constant at ~(1–2) × 10^3 s^{-1} for the samples, whereas k_{nr} values span several orders of magnitude.

Possible quenching mechanisms for the weakly emissive and nonemissive samples include excited-state energy transfer (Cu^{2+}, Eu^{3+}, and $Cr(urea)_6^{3+}$ derivatives), electron transfer (Ag^+ and Cu^{2+} derivatives) and H-atom abstraction ($n\text{-}C_4H_9NH_3^+$ and $n\text{-}C_8H_{17}NH_3^+$ derivatives). Partially Eu-substituted HUP provides evidence for excited-state energy transfer: both the UO_2^{2+}-based emission and pink Eu^{3+} luminescence are simultaneously observed upon excitation of of the UO_2^{2+} chromophore. The relative intensities of the two types of emission vary with the Eu content in both this system and Eu-substituted $Ca_{1/2}UP$ samples. Concentration effects on luminescence have also been investigated with Ag-substituted KUP. The UO_2^{2+}-based emission is partially quenched in samples prepared from solutions in which the Ag:K ratio is as little as ~1:10,000. Some evidence for an exciton mechanism has been obtained in these studies.

Derivatives of HUP based on cationic transition metal complexes such as $Cr(urea)_6^{3+}$ afford interesting comparisons of excited-state properties with solution environments. To illustrate, the Cr complex exhibits fluorescence and phosphorescence at 77 K in an EPA glass. Absorption bands due to this complex are relatively unaffected when the complex is incorporated into the HUP lattice (λ_{max} ~ 625 nm), but no emission is observed from the solid at 77 K. These observations illustrate the role of environment on excited-state processes and the versatility of HUP as a host lattice for evaluating environmental effects.

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The Electronic Structures of Adducts of Lanthanide(III) Tricyclopentadienides

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Adducts of the rare earth tricyclopentadienides ($Cp_3Pr\cdot add$) were first described by Birmingham and Wilkinson in 1954. Since then their chemistry and geometrical structures have been extensively studied. Although excellent optical spectra were reported by Pappalardo *et al.* at the end of the sixties, nothing is known about their electronic structures. The main reason for this is that they don't crystallize into single crystals which are suitable for optical measurements. Therefore they can only be studied in solution and the additional information obtained from polarized optical single crystal measurements is missing. In solution comparable information may be obtained by performing magnetic circular dichroism measurements.

By studying the cold and hot MCD transitions, 14 crystal field levels of $Cp_3Pr\cdot CNC_6H_{11}$ could be identified. After fitting this truncated crystal field splitting pattern, 36 bands in the low temperature absorption spectrum could be assigned. By fitting the energies of these 36 levels, a refined set of parameters was obtained. On the basis of this parameter set the low temperature absorption spectra of the adduct $Cp_3Nd\cdot MeTHF$ could also be explained.

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^{11}B NMR Studies on some Uranium(IV) Poly(pyrazol-1-yl) Borate Complexes

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Although no full X-ray structural data are available yet for the actinide complexes of the poly(pyrazol-1-yl)borates, a good deal of information has been obtained from their electronic and ^1H NMR spectra.

In this work results from ^{11}B NMR spectroscopy will be presented and a correlation with the above data is attempted. The compounds studied were of the type $UCl_x[H_nBL_{4-n}]_{4-x}$ where L = pyrazole or 3,5-dimethylpyrazole.

In spite of the broad lines observed in these compounds, the spectra are simple, and in some cases the large chemical shifts of some paramagnetic species seem to be quite helpful.

The spectra of the compounds $UCl_2[HB(3,5Me_2\text{-}Pz)_3]_2$ and $UCl_2[H_2B(3,5Me_2Pz)_2]_2$ in tetrahydrofuran display two lines, one with a small isotropic shift and another with a large isotropic shift. Titra-

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tions of UCl_4 in tetrahydrofuran with the corresponding potassium salts were followed simultaneously by ^{11}B NMR spectroscopy, electronic absorption spectroscopy and by conductivity measurements. In one of the experiments an intermediate species was found as shown by the ^{11}B NMR spectrum.

The first ^{11}B NMR variable temperature measurements of poly(pyrazol-1-yl)borates were made with the second compound dissolved in toluene and showed a Curie Weiss behaviour for one paramagnetic species.

In contrast with the above two compounds which show two ^{11}B NMR distinct lines, all the other analogous compounds studied, display only a single line.

Results from T_1 measurements obtained by the inversion recovery method will also be presented for the ligands and for some uranium species.

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^1H and ^{13}C Nuclear Magnetic Resonance Study of the Complexation of Uranyl Ion with (D)-Tartaric Acid

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The interaction of uranyl ion with tartaric and malic acids has been studied by means of the potentiometric method in the pH range 2–8 [1]. However a full pH range study of uranyl–malic acid complexation by NMR reveals the existence of more species [2]. This is also the case reported here. At least four uranyl–tartrate complexes are identified in ^1H (at 80 and 300 MHz) and ^{13}C (at 20 MHz) spectra. At low pH the ligand is mono or bidentate while at higher pH values tridentate chelates are dominating. Work is in progress to establish the stoichiometry of these complexes and to elucidate the exchange phenomena involving the various species present.

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B25

Variable Pressure NMR and Spectrophotometric Study of Lanthanide Solvation in DMF

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The equilibrium $[Ln(DMF)_8]^{3+}$ + DMF $\rightleftarrows$ $[Ln(DMF)_9]^{3+}$ has been studied in solutions of lanthanide perchlorates. For Nd the following thermodynamic parameters were obtained from spectrophotometric studies: $\Delta H = -14.9 \pm 13.$ kJ mol^{-1}, $\Delta S = -69.1 \pm 4.2$ J K^{-1} mol^{-1} and $\Delta V = -9.8 \pm 1.1$ cm^3 mol^{-1}. The NMR study of Ln = Ce–Nd and Tb–Yb shows that the proportion of the nine coordinate solvates rapidly becomes insignificant across the lanthanide series. Characteristic ^{17}O, ^{13}C and ^1H NMR shifts for $[Ln(DMF)_8]^{3+}$ are also reported.

Kinetic parameters for the exchange of DMF on $[Ln(DMF)_8]^{3+}$ (Ln = Tb–Yb) have been determined in neat DMF, by variable temperature and pressure ^1H- and ^{13}C-NMR at 1.4, 4.7 and 8.5 Tesla. For the high field high pressure experiments, a high resolution multinuclear probe fitting into the tubular wide-bore 4.7 Tesla superconducting magnet was built. The probe works between –60 to +130 °C and has been used to 250 MPa. The spectral resolution measured by ^1H-NMR is about 1 Hz, that is 5×10^{-9}. For the DMF exchange on Tb, the activation parameters, ΔH^* (kJ mol^{-1}), ΔS^* (J mol^{-1} K^{-1}) and ΔV^* (cm^3 mol^{-1}), are respectively, 14.1 ± 0.4, -58 ± 2 and $+5.2 \pm 0.2$ whilst for Yb the corresponding values are 39.3 ± 0.6, $+40 \pm 3$ and $+11.8 \pm 0.4$. The observed systematic variations in activation parameters from Tb to Yb are interpreted in terms of a mechanistic crossover at Er. Kinetic rate law determinations in CD_3NO_2 diluent indicate that an interchange mechanism operates for Tb (k_{os} = 0.5 at 231 K) whereas a D mechanism is operative for Yb.